Electrical Properties of molten TiO_2 - SiO_2 - Al_2O_3 - MgO - CaO slag

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Motivation

In New Zealand, molten TiO_2 – SiO_2 – Al_2O_3 – MgO – CaO slag is available as the by-product of the local ironmaking process.

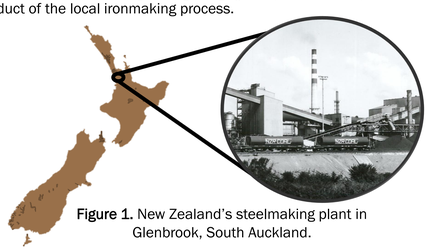


Figure 1. New Zealand's steelmaking plant in Glenbrook, South Auckland.

Recently, the electrochemical recovery of metals from this molten slag has been proven feasible [1]. However, a deeper understanding of the electrochemical behaviour of this complex oxide system, in its molten state, is paramount in the design of industrial electrolytic cells. The purpose of the present study is to quantify the contribution of the ionic and electronic charge carriers to the total electrical conductivity.

Methodology

The pendant droplet technique was used alongside iridium in a three-electrode configuration to perform electrochemical techniques inside a modified thermal imaging furnace. This containerless approach avoided any containment contamination [2].

Three compositions of a synthetic molten TiO_2 – SiO_2 – Al_2O_3 – MgO – CaO slag (see Table 1) were prepared using reagent grade powders [1]. The compositions studied are representative of Ti-bearing slag formed in the ironmaking process in New Zealand. The TiO_2 concentration has been lowered, while keeping the relative amounts of the other oxides approximately constant, to simulate a process where only titanium is continuously extracted from the slag.

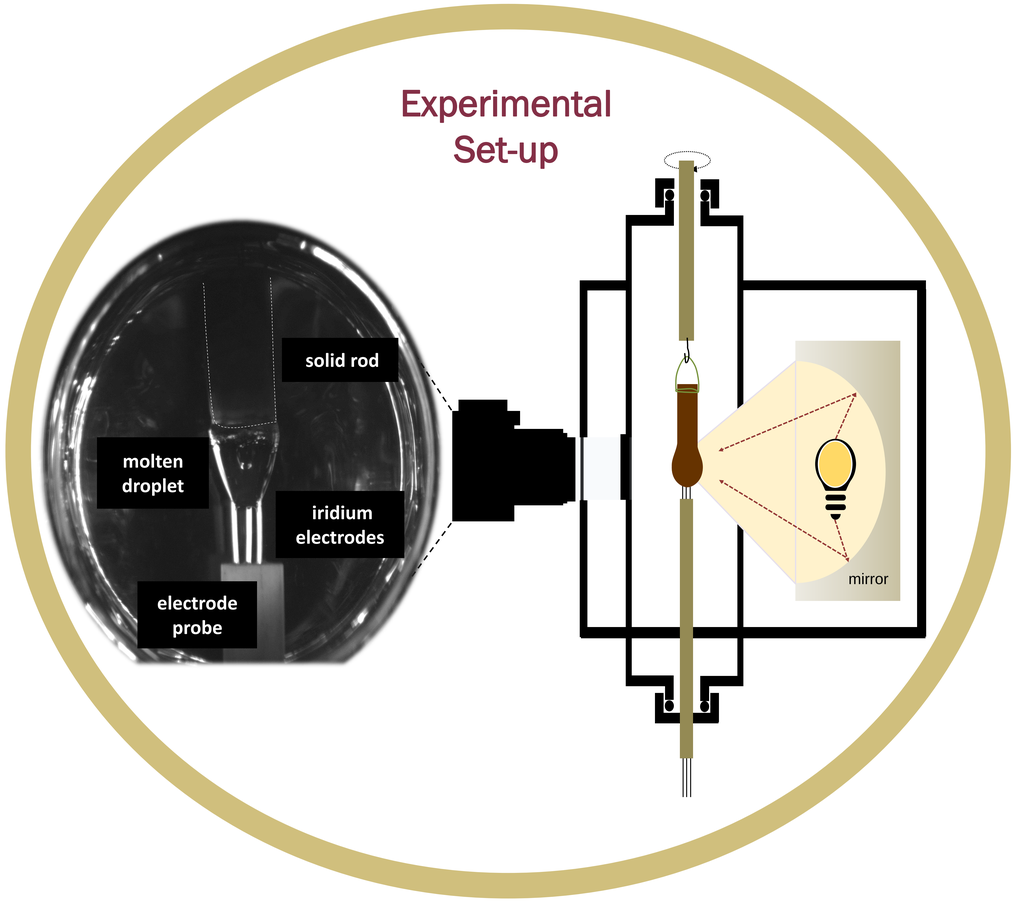
The solidus temperature (T_{sol}), and the liquidus temperature (T_{liq}) were predicted as a function of temperature using the thermodynamic software FactSage 7.2 [3] and validated, in previous work from this group [1], using differential scanning calorimetry and *in situ*, high temperature x-ray powder diffraction.

Table 1. Electrolyte compositions (wt.%) measured by XRF in ascending order of their predicted liquidus temperature.

	TiO_2 wt.%	CaO wt.%	SiO_2 wt.%	Al_2O_3 wt.%	MgO wt.%	T_{sol} K	T_{liq} K
Slag A	33	18	15	19	15	1486	1803
Slag B	15	24	25	18	18	1494	1823
Slag C	9	25	26	20	19	1494	1883

To quantify the partial electronic (σ_e) and ionic (σ_i) contributions to the total electrical conductivity (σ, S cm^{-1}), the electronic (t_e) and ionic (t_i) transference numbers were obtained from stepped-potential chronoamperometry experiments [4].

$$\sigma_{i/e} = \sigma \cdot t_{i/e}$$



Results

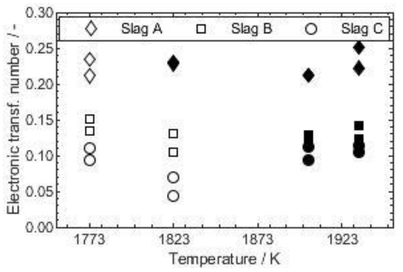
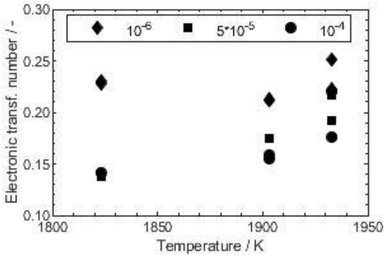


Figure 2. Electronic transference number variation with temperature for different partial pressures of oxygen (atm) for Slag A.

Figure 1. Electronic transference number variation with temperature for Slag A, Slag B and Slag C (33, 15, and 9 wt.% TiO_2, respectively). Measurements below the predicted liquidus temperature, T_{liq}, are presented with open symbols.



Discussion

The dependence of the transference numbers on the following parameters was studied to: (a) quantify the fraction of current carried by ionic or electronic charge carries, and (b) to investigate the small polaron conduction mechanism associated with metallurgical slags [5], including other molten transition metal bearing slags [6].

Effect of TiO_2 Content

Fried et al. [4] identified titanium's multivalence as responsible for the increase in electronic conduction, facilitating charge hopping. As the concentration of titanium cations increases in the melt, the easier it becomes to find a neighbouring ion, and an increase in the electronic conduction is expected. Accordingly, the electronic transference number was highest for the slag with the highest TiO_2 concentration (see Figure 1).

Effect of Oxygen Potential

For all the measurements performed above the T_{liq}, the electronic transference number increased with a decrease in the oxygen potential (see Figure 2). Lower oxygen potentials favours the reduction of Ti^{4+}, increasing the concentration of Ti^{3+} in the melt. This contributes to the increase in the electronic transference number as Ti^{3+} creates holes in the valence band, increasing electronic conduction [7].

Effect of Temperature

Temperatures around T_{liq} were chosen to investigate the effect of multi-phase conditions on the transference numbers (see Figure 1). Above the T_{liq}, the effect of temperature on electronic conduction was negligible, which is consistent with previous reports [6]. In the two-phase region, the solid phase fraction decreases with increasing temperature, which facilitates ionic mobility. That, consequently, caused the initial decrease in the electronic transference number.

Effect of Melt Structure

Ionic conduction strongly depends upon structure as free ions in the slag are the only ionic charge carriers. For the slags studied, as the degree of depolymerization and viscosity of the melt were nearly constant within the temperature and composition range measured [8], the influence of structure in the ionic conduction was minor.

Conclusions

The electronic transference number of the different slags ranged from 0.04 to 0.25 and was found to vary mainly with oxygen potential and total titanium content. This is consistent with the diffusion-assisted charge transfer model recently used to explain electronic conduction on molten FeO_x bearing slags [6].

References

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